# An $Al_{12}R_8^-$ cluster as an intermediate on the way from aluminium(I) compounds to aluminium metal†

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**A new $Al_{12}$ cluster resembling a small section of the aluminium lattice has been prepared by the reaction of AlCl solution with $LiN(SiMe_3)_2$.**

Metastable aluminium monohalide solutions generated *via* condensation of high temperature AlX molecules[1] have proved to be potential precursors for the synthesis of aluminium atom clusters. Besides $Al_4Cp^*_4$[2] as the first example, recently an $Al_{77}$ cluster[3] was prepared which is the largest metal atom cluster characterised by X-ray structure determination to date. In order to understand the formation of the $Al_{77}$ cluster that may be viewed as one of the final steps in the reaction pathway to the bulk metal, we attempted to isolate smaller intermediates. Very recently we were able to characterise an $Al_7R_6^-$ species with a unique $D_{3d}$ structure containing a 'naked' Al atom 'sandwiched' by two $Al_3R_3$ ring systems.[4] Here we report the cluster anion $Al_{12}R_8^-$ [R = $N(SiMe_3)_2$] which may be the next step on the way to the $Al_{77}$ cluster.

Black crystals of $Li(OEt_2)_3^+[Al_{12}\{N(SiMe_3)_2\}_8]^-$ **1** were formed after heating an $LiN(SiMe_3)_2$–AlCl solution (toluene–diethyl ether) to *ca.* 60 °C and subsequently storing at room temperature for 10 days (Scheme 1).‡

29 AlCl + 26 LiN(SiMe₃)₂

⟶ 24 LiCl + 2 Li⁺[Al₁₂{N(SiMe₃)₂}₈]⁻ + 5 [Al{N(SiMe₃)₂}₂]Cl

**1**
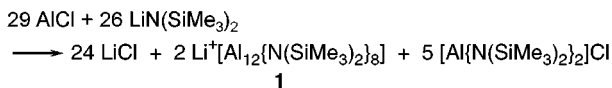
**Scheme 1**

In comparison to the $Al_{12}$ cluster, the $Al_7$ cluster [4] is formed by the same reaction under milder conditions (24 h at 20 °C and several weeks at −25 °C).

The structural result of the X-ray structure determination of **1** is shown in Fig. 1.§ The structure of the $Al_{12}[N(SiMe_3)_2]_8^-$ anion is similar to that of a neutral $In_{12}R_8$ cluster compound (R = $SiBu^t_3$) published recently by Wiberg *et al.*[5] The EPR spectrum of a solid sample of **1** confirmed the radical character of the anion. Like the $In_{12}$ cluster, the anion of **1** can be regarded as a section of the metal lattice as indicated in Fig. 2.

In order to understand the formation of the negatively charged $Al_{12}$ cluster in contrast to the neutral $In_{12}$ molecule preliminary DFT calculations[6] were performed for the species $In_{12}H_8$, $In_{12}H_8^-$, $Al_{12}H_8$ and $Al_{12}H_8^-$. The bonding situation for the $In_{12}$ and $Al_{12}$ cluster compounds is comparable in the following sense: addition of a single electron mostly influences the two apical Al3–Al5 bonds. This is evident by inspection of Table 1 which lists the calculated Al–Al distances of the model compounds $Al_{12}H_8$ and $Al_{12}H_8^-$. The discrepancies with respect to the observed distances in **1** disappear if $NH_2$ ligands are applied in place of H, *e.g.* for $Al_{12}(NH_2)_8^-$.[7] However, to obtain a complete insight into the electronic structure, extensive calculations including incorporation of $N(SiMe_3)_2$ ligands and without any symmetry restrictions have to be performed.

Calculations for the $In_{12}$ compounds revealed similar trends and the $In_{12}R_8^-$ anion should be also a stable species. However,

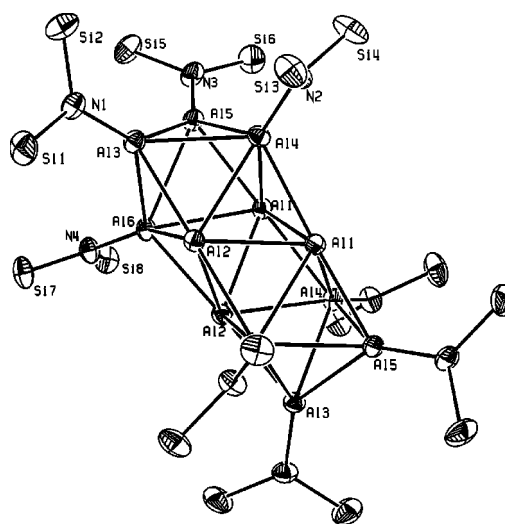† Dedicated to Professor Nils Wiberg on the occasion of his 65th birthday.



**Fig. 1** Molecular structure of **1** (50% probability thermal ellipsoids; methyl groups are omitted for clarity). Selected distances (pm): Al–Al (see Table 1), Al–N 184.8 (av.), N–Si 174.4 (av.).
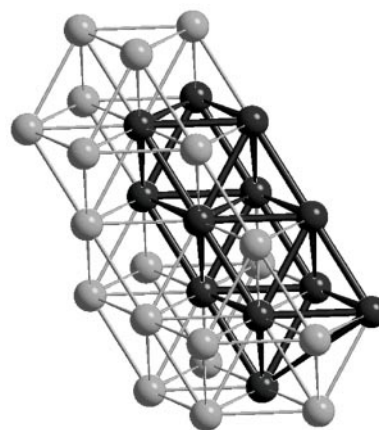


**Fig. 2** Section of the aluminium metal lattice (ccp); an $Al_{12}$ unit is accentuated.

**Table 1** Selected Al–Al bond lengths for $Al_{12}[N(SiMe_3)_2]_8^-$ **1** (experimentally determined) as well as $Al_{12}(NH_2)_8^-$ ($S_4$), $Al_{12}H_8^-$ ($D_{2d}$) and $Al_{12}H_8$ ($D_{2d}$) (calculated)

| $d$/pm | $Al_{12}[N(SiMe_3)_2]_8^-$ | $Al_{12}(NH_2)_8^-$ | $Al_{12}H_8^-$ | $Al_{12}H_8$ |
|---|---|---|---|---|
| Al1–Al5 | 259.8 | 259.4 | 254.3 | 251.4 |
| Al2–Al6′ | 268.2 | 266.1 | 270.0 | 272.4 |
| Al3–Al5 | 254.2 | 253.3 | 263.5 | 278.3 |
| Al3–Al6 | 279.9 | 275.2 | 269.2 | 267.9 |
| Al1–Al1′ | 263.0 | 273.3 | 271.6 | 270.2 |
| Al1-Al4' | 278.8 | 273.9 | 277.3 | 279.9 |

the higher electron affinity of $Al^+$ relative to $In^+$ may be the reason for its higher tendency to achieve a lower oxidation state (between 1 and 0): the average oxidation state of the Al atoms in $Al_{12}R_8^-$ is +0.58 while a value of +0.66 is found for In in $In_{12}R_8^-$.

20 triangular faces are present in **1** as also found in the well known $Al_{12}$ species $Al_{12}R_{12}^{2-}$ (R = $Bu^i$) with icosahedral symmetry.[8] Such a related *closo* $Al_{12}R_{12}^{2-}$ anion may be one of the primary intermediates during the formation of **1**. If 2 $R^-$ groups are removed from such an intermediate, an $Al_{12}R_{10}$ species will be formed which is similar to the distorted icosahedral $Al_{12}(AlBr_2)_{10}$ that we have published recently.[9]

$$Al_{12}R_{12}{}^{2-} \xrightarrow{-2R^-} Al_{12}R_{10} \xrightarrow{+2e^-, -2R^-} Al_{12}R_8 \xrightarrow{+e^-} Al_{12}R_8{}^-$$
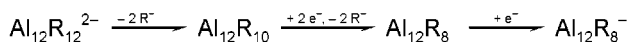
**Scheme 2**

Further reduction to $Al_{12}R_{10}^{2-}$ and dissociation of two additional $R^-$ ligands would lead to an $Al_{12}R_8$ molecule or the corresponding anion observed here. Since similar cluster compounds are obtained for In and Al, the proposed mechanism may represent the general pathway during reduction processes leading to the bulk metal. Therefore, intermediates similar to **1** can also be expected for other metals. However, the size of the metal atoms must be compatible with the size of the ligands, *i.e.* the large supersilyl ($SiBu^t_3$) ligands are suitable for protecting the large $In_{12}$ cluster whereas the smaller $N(SiMe_2)_2$ groups match the smaller $Al_{12}$ cluster.

Owing to the radical character of **1**, further physical measurements are underway in order to obtain more detailed information about the electronic structure of this $Al_{12}$ cluster compound which is an example of a metal atom cluster in the sense first stated by Cotton;[10] *i.e.* an assembly of metal atoms which are essentially connected by direct bonds. The presence of metal–metal bonds has been a primary reason for the increasing interest in metal cluster chemistry over the last two decades. However, while most ligand stabilised clusters published so far do not fulfil the original criterion of Cotton, **1** is a archetypal metal atom cluster since four or six Al atoms are directly bonded to each Al atom. Furthermore, in **1** the number of ligands is smaller than the number of metal atoms and no bridging ligands are present. In our opinion these latter two criteria should be fulfilled in order to regard a compound as a genuine metal atom cluster.

## Notes and references

‡ *General considerations*: all experiments were carried out under dry argon in a glovebox (Mbraun MB 150-GI) or under dry nitrogen using standard Schlenk techniques. Solvents were dried over potassium and degassed prior to use. EPR spectra were recorded on a BRUKER ESP 300 E.

*Synthesis*: 8.6 ml cold (−78 °C) AlCl solution (0.29 M, toluene–$Et_2O$) (2.5 mmol) was added dropwise to 500 mg (3.0 mmol) solid $LiN(SiMe_3)_2$. The reaction mixture was then heated quickly to 60 °C and stored for 2 h at this temperature. Subsequently, the dark brown solution was separated from solid LiCl. Storing at room temp. gave black crystals of **1** after 10 days. Yield in crystalline form: 11 mg (0.006 mmol) 28%; EPR (solid) $g_\perp$ = 2.015 ($\Delta B_{1/2}$ = 38.9 G), $g_\parallel$ = 2.23 (weak).

§ *Crystal data*: $C_{60}H_{152}Al_{12}LiN_8O_3Si_{16}$ **1**, $M$ = 1836.2, monoclinic, space group $P2/n$, $Z$ = 2, $a$ = 20.893(2), $b$ = 13.0123(10), $c$ = 21.455(2) Å, $\beta$ = 98.134(11)°, $V$ = 5774.5(9) Å$^3$, $\mu$(Mo-K$\alpha$) = 0.30 mm$^{-1}$, $T$ = 213(1) K, 31005 reflections collected/10283 ($R_{int}$ = 0.0600) independent/6348 with $I > 2\sigma(I)$. The structure was solved by direct methods and refined by full-matrix least squares on $F^2$ to final values of $R1[F > 4\sigma(F)]$ = 0.0553 and $wR2$ = 16.83 (all data). The diethyl ether molecules co-ordinated to the Li atom are strongly disordered. In treatment of this disorder we disregarded occupancies for hydrogen atoms. CCDC 182/1389. See http://www.rsc.org/suppdata/cc/1999/1933/ for crystallographic files in .cif format.

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7 For the radical anion $Al_{12}(NH_2)_8^-$ most of the calculated Al–Al distances are very close to those of **1**. A complete accordance with the experimentally determined structural data can not be expected since the $NH_2$ ligand is different from the $N(SiMe_3)_2$ group for the following reasons. (a) The N atom in the $NH_2$ group is pyramidally coordinated whereas a planar surrounding is observed for the $N(SiMe_3)_2$ groups. (b) The orientation of the $NR_2$ groups towards the $Al_{12}$ core should be different for both amide groups for steric reasons and therefore a different interaction of the lone pair of the N atom with the $Al_{12}$ core can be expected. In order to save computing time a symmetry restriction ($S_4$) was applied for the $Al_{12}(NH_2)_8$ species. The electron affinity for the process $Al_{12}(NH_2)_8 \rightarrow Al_{12}(NH_2)_8^-$ has been calculated to be exothermic by −145 kJ mol$^{-1}$.
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